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# Results of the Irradiation and Processing of Ultra-High Purity Sintered Natural Molybdenum Target Disks

**Nuclear Engineering Division** 

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# Results of the Irradiation and Processing of Ultra-High Purity Sintered Natural Molybdenum Target Disks

by

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	Mo disks		

### **1 INTRODUCTION**

A fine orange-brown powder was observed on the irradiated molybdenum (Mo) disks and on the target housing for irradiations that were performed in fiscal year (FY) 2015 [1, 2]. The source of the powder was later identified as coming from the helium (He) cooling loop and corrosion of the carbon (C)-steel shielding enclosure. After dissolution, light-orange-colored solutions were obtained and radiochemical purity (RCP) tests using thin-layer chromatography (TLC) that were performed with the undiluted Mo solution [3, 4] did not meet the specifications of  $\geq$ 95% of activity at R<sub>f</sub> = 0.9 ± 0.1 (R<sub>f</sub> = retention factor). Possible explanations for the negative RCP tests were the introduction of impurities into the final Mo solution either by corrosion products from the He cooling loop or by stabilizers that were present in the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) that was used for dissolution [tin (Sn) stabilizer or phosphate stabilizer]. Therefore, in FY 2016, several irradiations were undertaken [5] with ultra-high-purity (UHP) natural Mo and Mo-100-enriched disks, without using the He cooling system. For those tests, the Mo disks were wrapped in aluminum (Al) foil and placed behind a converter. The irradiated disks were then dissolved in non-stabilized 30% peroxide or Sn- and phosphate-stabilized 50% peroxide. It was determined that even the  $2-3 \times$  excess of Sn-stabilized H<sub>2</sub>O<sub>2</sub> that is typically used for the dissolution of sintered Mo disks did not affect the radiochemical purity of the final product. In the case of Mo-100-enriched targets, impurities such as 540 ppm iron (Fe), 75 ppm tungsten (W), 65 ppm chromium (Cr), 39 ppm nickel (Ni), 15 ppm copper (Cu), and 11 ppm germanium (Ge) in enriched material also did not affect the RCP. The highly alkaline Mo solution in 5 M potassium hydroxide (KOH) required dilution with water to obtain good chromatographic behavior. The conclusions of the FY 16 report [5] indicated that the prospective cause of the radiochemical impurities in the FY 2015 irradiations was due to corrosion in the He cooling system and the introduction of impurities into the final Mo product. Therefore, in FY 2017, a significant cleanup of the He cooling system was performed and irradiation of UHP Mo disks was performed to test the radiochemical purity of the Mo product solution. The results of this cleanup effort and the irradiation of the UHP Mo disks are discussed in this report.

### **2 HELIUM SYSTEM CLEAN UP**

The cleanup of the helium was initiated because we saw the dust that was deposited on the target holder after irradiation and were planning to install a larger target which we did not want to contaminate with the rust. The helium cooling system is shown in Figure 1. It provides the means to remove the heat that was generated in the target by flowing high pressure gaseous helium through the target. The cooling system consists of a pressure vessel housing an electric motor and a roots blower to move helium through the cooling loop, an oil filter to guard the system against undesired oil droplets, heat exchangers to remove heat generated in the target and from compression of the gas in the blower, and a mass flowmeter for precise mass-flow measurements. Originally, we suspected that the rust was coming from the carbon steel shielding insert located under the target insertion port. After opening the target housing and examining the tubing that was directly connected to the target housing we did not find a significant amount of



FIGURE 1 Helium cooling system.

dust that would explain the target contamination. After the complete disassembly of the cooling loop, we found that the oil filter was covered in rust (see Figure 2) on the inside, and part of the system from the roots blower to the oil filter was contaminated with oil from the blower gearbox (see Figure 3). All components of the cooling system were examined and cleaned. The roots blower was replaced, the filter elements in the oil filter were replaced, and all of the rust was removed and the surfaces were coated with paint.



FIGURE 2 Inside view of the oil filter. Rust is visible on all internal surfaces of the filter body before (top two pictures) and after cleanup (bottom picture, all exposed surfaces are painted).



FIGURE 3 Extent of the oil contamination in the helium cooling system.

### **3 IRRADIATION PARAMETERS**

This irradiation run was performed at 40 MeV beam energy. The linac's spectrometer has an upper limit for beam energy measurements of 40 MeV; therefore, the beam energy profile tuning was performed at 38 MeV (see Figure 4) corresponding to the 0.6 A injector current. After that, the injector current was lowered to 0.55 A to reduce the beam load for the accelerating structure which increases the energy gain of the electron beam to 40 MeV according to the linac's load-line data [1]. The transverse beam size was adjusted to  $5.4 \times 5.5$  mm using optical transition radiation (OTR) detected with a charge-coupled device (CCD) camera (see Figure 5).

Beam focusing and alignment were performed with a low repletion rate (low beam power of about 0.2 kW). After that, the repetition rate was slowly increased to 95 Hz, which corresponds to an average beam current of about 225  $\mu$ A and an average beam power of about 9 kW (see Figure 6). Indirect thermal measurements of the target window were made with a FLIR® A655sc-70 infrared (IR) camera with high-temperature calibration. The full-window frame rate of the camera is 50 Hz. For these experiments, frame data were saved every 10 seconds. We kept the temperature of the target window below 600°C during the whole irradiation time.



FIGURE 4 Energy spectrum of the beam.



FIGURE 5 Optical transition radiation beam image at the target window. The diameter of the blue circle is 12 mm.

The average beam power was monitored during the experimental run with fast current transformers (FCTs). The cause of some variation of the power is due to the injector's thermal cathode instability. Keeping the power in the desired range required periodic correction by the linac operator. The beam power history for the duration of the experiment is presented in Figure 6. The total duration of the irradiation was 22.5 hours with a few short interruptions due to arching in the accelerator structures.





FIGURE 6 Beam power history. The red line, on Figure 6 a, represents beam power at the accelerator exit. The blue line, on Figure 6 b, represents beam power near the target.

### **4 POST-IRRADIATION TARGET PROCESSING**

Target assembly containing 25 natural Mo disks (six disks were sintered and ultra-high purity, the remaining 19 disks were metallic Mo disks) after irradiation is shown in Figure 7. It was observed that white powder was present on the target. The source of the white powder is unknown.

The irradiated UHP Mo disks (5.8 g) were dissolved in 50% H<sub>2</sub>O<sub>2</sub> stabilized with phosphate (Fisher Scientific H311-500, Lot #162233). After a complete dissolution, an orange-colored solution was obtained. Then 8.5 g of KOH (Sigma Aldrich, part # P1767-2KG) dissolved in ~6 mL of water was added to convert the Mo to potassium molybdate (K<sub>2</sub>MoO<sub>4</sub>) (see Figure 8). The excess H<sub>2</sub>O<sub>2</sub> and water were eliminated by evaporation and allowing it to cool. Then ~0.3 mL of 1 M Fe(NO<sub>3</sub>)<sub>3</sub> was added for the removal of zirconium (Zr) and



FIGURE 7 An unidentified white powder was visible on the target after irradiation.

niobium (Nb) by coprecipitation. The precipitate was removed by filtration using a 0.3  $\mu$ m 40 mm polyvinyl difluoride (PVDF) filter. A clear and colorless solution was obtained after the filtration was combined with 9 g of solid KOH, and the final volume was adjusted to 29 mL by adding water to make the solution of 0.2 g Mo/mL in a ~5 M KOH solution.



FIGURE 8 Dissolution setup. Left: Orange-colored solution obtained after the complete dissolution of UHP Mo disks in 50% peroxide (circled in blue on the left picture). Right: Colorless solution obtained after the addition of KOH to convert the Mo into K<sub>2</sub>MoO<sub>4</sub> (circled in blue on the right picture).

A small aliquot of the final Mo solution was gamma counted to determine the Mo activity and presence of the other side reaction by-products. The gamma counting results are shown in Table 1.

Radionuclide	Activity at EOB, mCi	2 sigma uncertainty	After filtration % of Mo-99
N. 00	252.25	0.100/	1000/
Mo-99	352.35	0.10%	100%
Nb-92 m	0.50	1.30%	0.14%
Nb-95 m	8.27	0.57%	2.35%
Nb-95	0.79	0.85%	0.23%
Nb-96	18.62	0.40%	5.28%
Zr-95	MDA	NA	NA

TABLE 1 Gamma counting results for irradiated 5.8 g of ultra-high puritymolybdenum Mo disks.

25 mL of the final Mo solution containing ~200 mCi of Mo-99 at the time of shipment (Wednesday, May 17, 2017 at 9 a.m.) was loaded into a shipping vessel and shipped to NorthStar for further processing. One day after the dissolution, a radiochemical purity test was performed by loading 10  $\mu$ l of 5 × diluted Mo solution on a paper chromatogram with ITLC-SG strips (Agilent Technologies SGI0001). The chromatograms were developed in a 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution. Since the solution is colorless, the front of the thin-layer chromatography (TLC) was marked with a droplet of phenolphthalein to visually diagnose when the mobile phase reached the front of the chromatogram. This was indicated by a purple color on the front of the chromatogram (see Figure 9). After development, the TLC strips were allowed to dry, cut into 11 fractions, and gamma counted. Gamma counting was performed with a high-purity germanium (HPGe) detector.

The retention factors ( $R_f$ ) of Mo-99 and Tc-99m were  $R_f=0.9\pm0.1=99.2\%$  and 98.4% for Mo and Tc, respectively. Based on the RCP results (see Figure 10) the solution met the radiochemical purity specifications.



FIGURE 9 Spotting of mobile phase (Na<sub>2</sub>CO<sub>3</sub>) on thin-layer chromatography (TLC) using phenolphthalein.



FIGURE 10 Retention factors for Mo and Tc, after spotting 20  $\mu$ L of 5 × diluted solution of Mo in 5 M KOH on thin-layer chromatography (TLC) and eluting it in 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution.

# **5 CONCLUSION**

Based on the irradiation with the UHP Mo disks and the RCP test, it was determined that the corrosion products (rust) present in the helium (He) cooling loop in previous Argonne irradiations of Mo-100 enriched targets was the reason for the radiochemical impurities due to their possible interaction with Mo and Tc in the final product solution. After the thorough cleanup of the He cooling system, the irradiation and dissolution of the UHP Mo disks with 50% peroxide (phosphate stabilized) RCP test showed that both the Mo and Tc met the specifications (>95% of activity at  $R_f=0.9\pm0.1$ ).

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